

# CASE STUDY OF WATER POLLUTION IN PODWIŚNÍÓWKA ACID MINE PIT LAKE (HOLY CROSS MTS., POLAND)

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**ABSTRACT:** On the Holy Cross Mountains (southern Poland), located within the tectonic zone of the Trans-European Suture Zone (TESZ), numerous former quarries exist, including those of Cambrian quartzitic sandstones and sandstones with pyrite veins. This article presents the results of geochemical studies on the waters of the acidic mine pit lake Podwiśnówka (with an area of 1.5 ha and a maximum depth of 7.0 m) conducted in 2018. The tests were carried out in a vertical water column (every 1 m) in the central part of pit lake. The mean concentration of metals/metalloids, determined using inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS), was found to form the following sequence in decreasing order: As > Cu > Ni > Co > Cr > Zn > U > Pb > Cd > Tl. With increasing depth, there was a general upwards trend in the concentrations of all the determined elements. In all cases, the average value of the single pollution index in the water column greatly exceeds the very strong level in relation to the geochemical background of surface waters globally (As – above 1250 times). The integrated pollution index for the ten trace elements in the water column increases with depth, and its average value exceeding 250 times the highest reference level. At the same time, the cluster analysis carried out showed the existence of two distinct depth zones in the pit lake: upper (0–4 m) and lower (5–7 m), differing in the scale of the water pollution.

**KEYWORDS:** acidic mine pit lake, water pollution indices, trace elements, arsenic

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## Introduction

Many post-mining excavations fill with water and become interesting hydrographic objects (Ramstedt et al. 2003, Pellicori et al. 2005, Balistrieri et al. 2006, Hrdinka et al. 2013, Schultze 2013, Tucci, Gammons 2015, Molenda, Kidawa 2020), and limnological studies conducted most often focus on identifying selected features of water chemistry (Moser, Weisse 2011, Pociecha et al. 2017, Żurek et al. 2018, Molenda et al. 2020,

Oszkinis-Golon et al. 2020). The physicochemical parameters of water in some lakes indicate a high level of toxicity, which poses a potential threat to the natural environment in their vicinity. This may be caused by high concentrations of some chemical compounds (Nordstrom 2011, Migaszewski et al. 2018a) and trace elements (Williams, Smith 2000, Migaszewski et al. 2016), together with the fact of the water in the lakes being characterised by low pH values. The sources of the toxic substances in the water are leached

minerals from parent materials occurring in both the underground and surface drainage of rock formations, especially in areas with a complex geological structure, both tectonically and lithologically. Additionally, metal sulphides, mainly pyrite (e.g. Karakas et al. 2003, Grawunder et al. 2014, Migaszewski et al. 2018a), create an exceptional situation. Very high concentrations of arsenic and other trace elements have been recorded in mine pit lakes worldwide (Sánchez-España et al. 2008).

The pit lake of this case study, Podwiśniówka, occupies a former quartzite sandstone quarry in the Holy Cross Mountains (southern Poland). According to Migaszewski et al. (2019), this lake is among the most unique in the world due to the extremely high concentration of pyrite in the surrounding sedimentary rocks, and has already been the subject of geochemical studies led by Migaszewski et al. (2007a, b, 2008). These authors found very high concentrations of trace elements, including arsenic, in the surface water and the

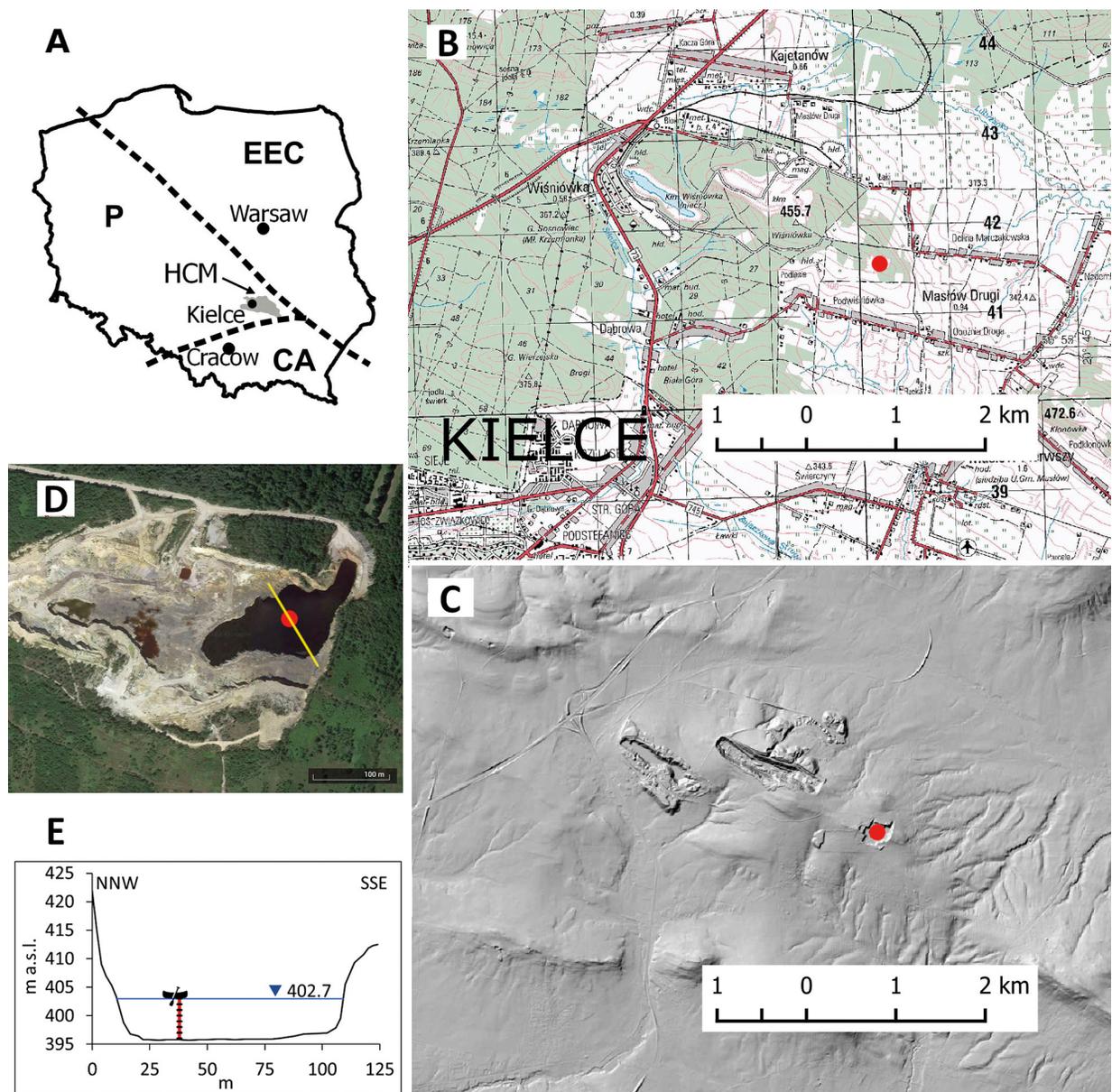


Fig. 1. Location of Podwiśniówka pit lake against A – significant geotectonic structures (Żylińska et al. 2006), namely Holy Cross Mountains (HCM), Precambrian East European Craton (EEC), Palaeozoic Caledonian and Variscan fold belt (P) and Carpathian Alpine orogenic belt (CA); B – a topographic map; C – Digital Elevation Model; D – orthophoto maps (<https://earth.google.com>); E – relief profile. The red dots in B–D and the boat symbol in E indicate measurements in the lake.

leachate. However, no geochemical study has been carried out in the vertical water column, and no assessment of water pollution has been made.

This study aims to assess the quality of the water in the acidic mine pit lake of Podwiśnówka based on an analysis of the concentration of 10 trace metals in the vertical water column using water pollution indicators.

## Study area

This case study examines the Podwiśnówka mine pit lake, which has an area of 1.58 ha, an average depth of approx. 6.4 m and a volume of 101,000 m<sup>3</sup>; this lake formation developed in 2014 in one of the former quarries in the Holy Cross Mountains. The mountains are located near one of the best-known geotectonic structures in Europe, i.e. the Trans-European Suture Zone (TESZ) (Berthelsen 1992, Nawrocki, Poprawa 2006), and on the border of three significant geological units (Lamarche et al. 2002): the Precambrian East European Craton (EEC), the Western European Platform of Palaeozoic consolidation (P) and the Małopolska Block in the zone of the Carpathian Alpine orogenic belt and basins (CA) (Fig. 1A, B).

There is a complex system of tectonic structures in the area, including the Holy Cross dislocation

and numerous transverse faults accompanied by hydrothermal phenomena (Kowalczewski, Dadlez 1996, Konon 2008). Within the quarrying area (4.1 km<sup>2</sup>), apart from the Podwiśnówka quarry, there are two more pits, the active Wiśnówka Duża and the closed Wiśnówka Mała. Over the preceding 12 years, numerous detailed geochemical studies investigating these pits have been conducted in the researches of Migaszewski and Gałuszka (2010) and Migaszewski et al. (2007b, 2013, 2018a). In the past, quartzitic sandstones from the Upper Cambrian (Furongian) with embedded mudstones, silt shales, tuffites and bentonites were quarried here. Together, they form the Wiśnówka sandstone formation (Filonowicz 1973, Żylinska et al. 2006).

The studied pit lake, which developed in the quarry (Fig. 1C, D, E and Fig. 2) in the immediate zone of pyrite mineralisation, is distinguished due to the very low pH (<3.0) (Migaszewski et al. 2018b).

## Materials and methods

### Water sampling and laboratory analysis

The basic physicochemical and chemical properties of mine pit lake water were



Fig. 2. Podwiśnówka mine pit lake (the boat indicates the site of measurement).

identified at distinct times of the year, while detailed hydrogeochemical tests were performed in November 2018 (during the autumn circulation). Measurements of the depth of the pit lake and the water were determined in the central part of the lake, directly from a pontoon using the YSI EDS 6600 multiparameter probe (Fig. 2). The water parameters were determined for a vertical column every metre in the central part of the reservoir. The transparency of the water was also tested with a Secchi disc.

Water samples for chemical analyses were collected directly into polythene bottles at 1 m intervals using an Eijkelkamp bathometer, with procedures preventing their contamination. Similar precautions were applied during the transport, storage and laboratory analyses' preparation process. Its filtration through a 0.45  $\mu\text{m}$  filter (Merck Millipore) preceded laboratory analyses of the chemical composition of water. The contents of selected cations and anions in the water,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , were determined using a Metrohm 850 Professional IC ion chromatograph, and the concentration of iron ( $\text{Fe}_{\text{tot}}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) and selected trace elements were determined using an inductively coupled plasma-quadrupole mass spectrometer (ICP-QMS; ELAN DRC II model, Perkin Elmer). For trace element determination, a set of solutions prepared from Multielement Calibration Standards (Perkin Elmer) were applied. The standard reference material (SRM) used for measuring metal/metalloid concentrations in the samples was NIST 1643e (trace elements in water). Quality control included both accuracy (SRM) and precision. The influence of physical interference was minimised using Rh and Ir as internal standards. The concentration of As was selectively controlled by the hydride generation atomic absorption spectrometry (HG-AAS) method using the iCE 3500Z spectrometer (Thermo Fisher Scientific).

## Water pollution assessment

The starting point for assessing the degree of pit lake water pollution was an analysis of the concentration of 10 elements (As, Cd, Co, Cr, Cu, Ni, Pb, Tl, U and Zn) at eight depths in the water column. An analysis of the correlation between the concentrations of selected metals was performed, including determining the significance level.

The degree of individual trace element contamination in water was determined using two methods: the single pollution index (SPI) and the integrated pollution index (IPI). They are easy to apply and omit the available ability of trace elements. The SPI is defined as the ratio of the metal concentration in the water sample to the background concentration of that metal (Kowalska et al. 2018):

$$SPI_i = \frac{C_i}{B_i} \quad [1]$$

where:

- $C_i$  represents metal content in water ( $\mu\text{g} \cdot \text{L}^{-1}$ ),
- $B_i$  represents reference values ( $\mu\text{g} \cdot \text{L}^{-1}$ ).

The calculations were based on the average concentrations of selected metals for global surface waters (Salminen et al. 2005) (Table 1).

The IPI was used to comprehensively evaluate the composite pollution conditions of different trace elements in the water column. They are calculated using the following equation (Taghipour et al. 2013, Qing 2015):

$$IPI = \frac{(SPI_1 + SPI_2 + \dots + SPI_n)}{n} \quad [2]$$

where  $n$  indicates the number of trace elements.

The following terminology was used for the pollution index model:  $SPI(IPI) < 1$ , non-pollution

Table 1. Global reference surface water values (Salminen et al. 2005) and for the upper continental crust (McLennan 2001).

Feature		U	Cd	As	Tl	Co	Cu	Ni	Pb	Cr	Zn
Reference values	Surface water - world [ $\mu\text{g} \cdot \text{L}^{-1}$ ]	0.5	0.2	2.0	0.01	0.3	7.0	2.5	0.3	1.0	20
	Rock - upper continental crust [ $\mu\text{g} \cdot \text{kg}^{-1}$ ]	2800	98	1500	750	17,000	25,000	44,000	20,000	83,000	71,000
	Standard WHO (2022) [ $\mu\text{g} \cdot \text{L}^{-1}$ ]	30*	3	10	-	-	2000	70	10	50	-

\* - provisional.

(absent);  $1 \leq \text{SPI(IPI)} < 2$ , low level of pollution;  $2 \leq \text{SPI(IPI)} < 3$ , moderate level of pollution;  $3 \leq \text{SPI(IPI)} < 5$ , strong level of pollution; and  $\text{SPI(IPI)} \geq 5$ , very strong level of pollution (Kowalska et al. 2018).

The listed indices were selected from the indicators for assessing the degree of metal contamination used in the literature. The research conducted on the subject of determining the degree of environmental pollution, as comprised in the literature, shows that it is most often defined concerning soils (Jiang et al. 2014, Chen et al. 2015, Karim et al. 2015, Mazurek et al. 2019, Wiczorek, Baran 2022), as well as river and lake sediments (Yan et al. 2016, Zhou et al. 2020). Few analyses of this type concern water in rivers and lakes (Yanguo et al. 2004, Islam et al. 2015, Zhaoyong et al. 2015, Liu et al. 2017, Dey et al. 2021, Pan et al. 2022).

## Results and discussion

### Major physicochemical characteristics of water

Research has shown that the water in Podwiśniówka pit lake is layered during the summer, which is characteristic of most lakes in the temperate zone (Fig. 3A).

In autumn, there is thermal equalisation (homothermia) and complete water mixing. In summer, a very rapid drop in water temperature with depth is observed (Fig. 3A). The epilimnion layer, characteristic of natural lakes, is not recorded

in water temperature even to a certain depth (Choiński 2007). The rapid drop in water temperature with depth (from 24°C to 8°C at a depth of 4 m) can be explained by the low water transparency, which is indicated by visibility from 0.7 m to 0.8 m determined by a Secchi disc, and this causes minimal penetration of solar radiation into the lake. The water in the lake has a characteristic ochreous colour. Below a depth of 4 m, the water temperature stabilised at 8°C. On the other hand, in autumn, the water temperature throughout the profile is even and amounts to approximately 8°C (Fig. 3A). However, despite the even temperature in the vertical profile in the autumn, homogenisation of the remaining physicochemical properties of the waters is not observed.

Corresponding to progression along the depth, the electrolytic conductivity of water shows very high values (Fig. 3B), and this is gauged as being the result of the accumulation of mineral substances, which have their source in the leachate flowing inwards from the quarry walls, in the lake, which represents an undrained body of water. The Cambrian rocks in the Podwiśniówka quarry contain metal sulphides, mainly pyrite (Migaszewski et al. 2007a, 2018b). The process of their weathering supplies the water entering the lake with a high concentration of sulphate and iron ions (Chowdhury et al. 1999, Bissen, Frimmel 2003, Kumari et al. 2017), and this phenomenon can be described by the following chemical reactions of pyrite weathering (Garrels, Thompson 1960, Alvarenga et al. 2021):

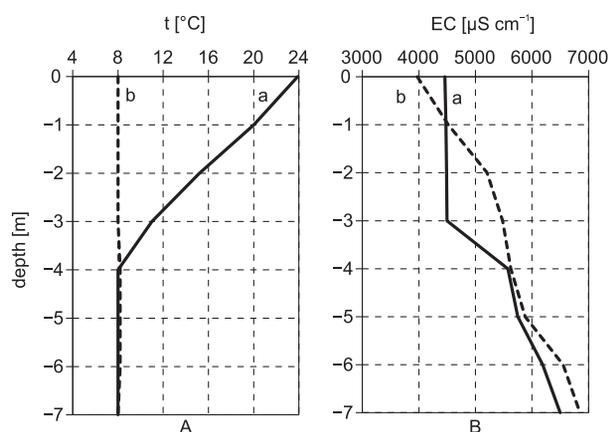
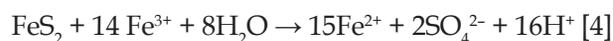
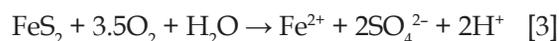


Fig. 3. Temperature – A and electrolytic conductivity – B of water in the vertical column of the mine pit lake during summer – a and autumn – b.

Migaszewski et al. (2007a, 2018b) found that the water in the leachate in the vicinity of the Podwiśniówka pit lake has a strongly acidic reaction (<2 pH) and very high electrical conductivity (EC) (>10,000  $\mu\text{S} \cdot \text{cm}^{-1}$ ). Values similar to these physicochemical parameters are found to characterise the watercourses draining this type of quarries, an example being the Água Forte in Portugal (Alvarenga et al. 2021).

In the near-surface layer of the Podwiśniówka pit lake, the value of EC ranges from 3970  $\mu\text{S} \cdot \text{cm}^{-1}$  (in autumn) to 4460  $\mu\text{S} \cdot \text{cm}^{-1}$  (in summer). The EC values were also far below the WHO (2022)

guideline value of  $800\text{--}1000 \mu\text{S} \cdot \text{cm}^{-1}$ . In the bottom layer, it reaches over  $6500 \mu\text{S} \cdot \text{cm}^{-1}$ . The lower EC in the near-surface layer is mainly due to the direct supply of low-mineralised rainwater and the inflow of surface runoff. The EC down to 3 m is uniform during the summer (approximately  $4460 \mu\text{S} \cdot \text{cm}^{-1}$ ), which indicates a zone of complete water mixing. At deeper depths (>3 m), an abrupt change is observed in EC (chemocline), followed by the stabilisation of its value (monimolimnion, Fig. 3B). A steady and apparent increase in the value of EC in the vertical column, observed in autumn (up to  $6850 \mu\text{S} \cdot \text{cm}^{-1}$  at the bottom), indicates a significant water mixing impediment. According to Boehrer et al. (2017), this impediment is demonstrative of the features of a meromictic lake. Similar processes have been observed in other lakes with high water mineralisation (Molenda 2011, 2018, Moser, Weisse 2011). The identified water stratification in the lake is permanent and occurs both in summer and autumn.

High mineralisation is reflected in the concentration of selected ions in the lake water (Table 2).

The concentrations of iron ( $\text{Fe}_{\text{tot.}} > 700 \text{ mg} \cdot \text{L}^{-1}$ ) and  $\text{Fe}^{2+}$  are significant here, which in the latter case increases more than 10-fold from the lake surface to its bottom (Table 2). A high concentration of sulphates ( $\text{SO}_4^{2-} > 3000 \text{ mg} \cdot \text{L}^{-1}$ ), which is a consequence of the weathering of pyrite, occurs in the entire water column of the lake and clearly (by approx. 10%) increases only at a depth of 6 m. These values were far above the safe limit ( $1000 \text{ mg} \cdot \text{L}^{-1}$  for drinking water) suggested by WHO (2022). A similar range of sulphate concentrations ( $2720\text{--}5460 \text{ mg} \cdot \text{L}^{-1}$ ) was found by Migaszewski et al. (2016) in the surface layer of this lake and by Moser and Weisse (2011) in the depth profile of the most acidified Austrian lake located at Langau, i.e. side lake of Bergwerkseen.

Table 2. Dry matter (TDS), salinity and concentration of selected ions in the water column (every 1 m) of the Podwiśniówka mine pit lake on 18 November 2018.

Depth [m]	TDS [ $\text{mg} \cdot \text{L}^{-1}$ ]	Salinity [%]	$\text{Fe}_{\text{tot.}} = \text{Fe}^{(3+)} + \text{Fe}^{(2+)}$	$\text{Fe}^{2+}$	$\text{SO}_4^{2-}$	$\text{PO}_4^{3-}$
			[ $\text{mg} \cdot \text{L}^{-1}$ ]			
0	2580	2.9	739	12	3110	16.2
1	2938	3.2	736	12	3110	13.3
2	3383	3.7	762	12	3090	11.6
3	3562	3.9	741	21	3000	15.6
4	3656	4.1	774	34	3060	14.2
5	3822	4.3	770	79	3090	15.3
6	4258	4.7	808	100	3460	15.6
7	4453	4.9	842	130	3390	18.4

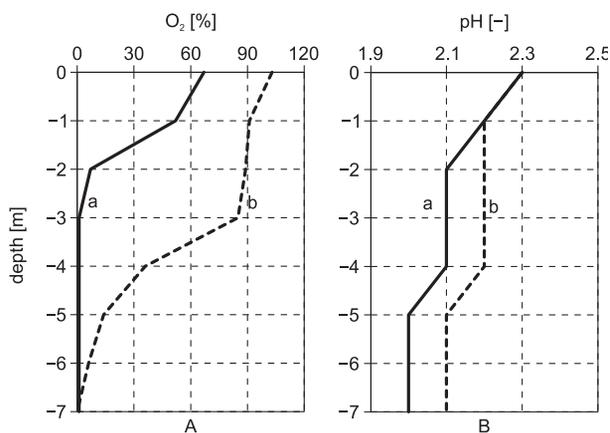


Fig. 4. Water saturation with oxygen – A and water pH – B in the vertical column of the mine pit lake: a – summer, b – autumn.

A good indicator of incomplete water mixing is the lake's oxygen condition (Fig. 4A). In summer, in the near-surface layer, the water saturation with oxygen is only 67%, and at a depth below 2 m, there are anaerobic conditions. More favourable oxygen conditions occurred in autumn when the water at depths <3 m was saturated at 85–103%, but the bottom layer was anaerobic (Fig. 4A). Better oxygen conditions (water saturation with oxygen) occurred in another acidic post-mining lake (Hromnicki) in northern Czechia (Hrdinka et al. 2013). In this case, the supersaturation of water with oxygen was caused by intensive photosynthesis processes.

The water pH has a low variability in the vertical water column, regardless of the measurement period (Fig. 4B). The surface layer waters (2.3 pH) show a slightly lower acidity than the bottom (2.0 pH). An explanation for this situation would be the rainfall, which is less acidic than the leachate water (pH < 2.0). Low pH values were also found in numerous streams from the pyritic quarrying area in Portugal (e.g. Luís et al. 2016, Alvarenga et al. 2021).

## Analysis of metal/metalloid concentrations in water samples

Using the calculation of the average concentrations of 10 metals/metalloids in the vertical column of water, their decreasing order was determined to follow the sequence  $As > Cu > Ni > Co > Cr > Zn > U > Pb > Cd > Tl$ . In general, along with the depth of water, there is an upwards trend in the concentration of all analysed elements, which is confirmed by the results of studies conducted in many lakes around the world (von Gunten et al. 2018, Canpolat et al. 2020, Lin et al. 2020). The distribution of concentrations of individual elements in the water column was similar (Fig. 5).

Arsenic results show it is highly concentrated. In the surface water layer, it amounts to  $11,833 \mu\text{g} \cdot \text{L}^{-1}$  and increases to  $13,818 \mu\text{g} \cdot \text{L}^{-1}$  at the bottom, i.e. at a depth of 7 m (Fig. 5). Similar changes were observed in the adjacent Wiśniówka post-mining lake (Molenda et al. 2020) resulting from the geochemical contact of these waters with the rocks of the Podwiśniówka quarry. The maximum concentration of As of  $3.05 \times 10^6 \mu\text{g} \cdot \text{kg}^{-1}$  was documented here in quartz-pyrite veins by Migaszewski et al. (2007b). The steepest As concentration increase in the vertical column in the central part of the water reservoir was found at a depth below 4 m. In lakes with thermal-oxygen stratification, according to Drewniak and Skłodowska (2013), arsenic circulates between the zones and bottom sediments, where it is sorbed by organic matter, aluminium and iron hydroxides. Microorganisms play an essential role in these processes. The high concentration of As in the water of this lake was previously stated by Migaszewski et al. (2016, 2018a, b). In 2014–2016, based on six water samples collected in the lake's coastal zone, the average As content was determined as  $15,416 \mu\text{g} \cdot \text{L}^{-1}$ , and in the leachate, as  $370,000 \mu\text{g} \cdot \text{L}^{-1}$ . The As concentration in the Podwiśniówka pit lake is tens of thousands of times greater than the natural arsenic levels ( $0.15\text{--}0.45 \mu\text{g} \cdot \text{L}^{-1}$ ) in global surface waters (Kumari et al. 2017). Interestingly, only in the water of the Corta Atalaya acidic mine pit lake in the Iberian Pyrite Belt was the concentration of As even higher –  $159,000 \mu\text{g} \cdot \text{L}^{-1}$  (Sánchez-España et al. 2008), one of the highest values recorded thus far in surface waters globally. High As concentrations

are also recorded in the waters of rivers draining catchments where mines currently exist (or operated in the past). The Reigous Creek (southern France) is an example of this high As concentration, where the maximum As concentration was  $264,000 \mu\text{g} \cdot \text{L}^{-1}$  (Giloteaux et al. 2013); other examples are Bone River (Indonesia),  $82,500 \mu\text{g} \cdot \text{L}^{-1}$  (Gafur et al. 2018); Zarshuran Stream (Iran),  $12,600 \mu\text{g} \cdot \text{L}^{-1}$  (Bakhshinezhad et al. 2019), and even  $40,000 \mu\text{g} \cdot \text{L}^{-1}$  (Modabberi, Moore 2004). In flowing waters in Poland, the highest concentration of arsenic ( $1700 \mu\text{g} \cdot \text{L}^{-1}$ ) was found in the watercourses flowing out of the abandoned arsenic ore mine at Złoty Stok (Mickiewicz et al. 2015) and below in the Trująca River at the level of approximately  $600 \mu\text{g} \cdot \text{L}^{-1}$  (Stachnik et al. 2020).

The element with the second highest concentrations in the Podwiśniówka lake water is Cu (average of  $5999 \mu\text{g} \cdot \text{L}^{-1}$ ), which exceeds approximately 480 times the value of the geochemical background of surface waters in Poland ( $12.5 \mu\text{g} \cdot \text{L}^{-1}$ ) and approx. 120 times the standard ( $50 \mu\text{g} \cdot \text{L}^{-1}$ ) established for these waters (Regulation... 2021). An even higher Cu concentration ( $68,795 \mu\text{g} \cdot \text{L}^{-1}$ ) was detected in the Aljustrel Mining Area stream (Luís et al. 2016). The average concentration of this metal in the rocks surrounding the Podwiśniówka mine pit lake is approx.  $2.0 \times 10^4 \mu\text{g} \cdot \text{kg}^{-1}$  (Migaszewski et al. 2007b). The high Cu concentration in the lake water indicates the intense dissolution processes of various copper compounds occurring here (e.g. chalcopyrite, covellite, tetrahedrite) (Migaszewski et al. 2019) in very acidic waters (Dojlido 1995). Migaszewski et al. (2016) showed that the Cu concentration in the surface water of the Podwiśniówka mine pit lake (in the initial stage of its development) was over  $14,000 \mu\text{g} \cdot \text{L}^{-1}$ . Research carried out a few years later on the water column shows that the Cu concentration varies from  $5489 \mu\text{g} \cdot \text{L}^{-1}$  (at the surface) to  $6574 \mu\text{g} \cdot \text{L}^{-1}$  (at the bottom). A significant increase in Cu concentration in the vertical water column was found, as is the case of As, at a depth of 4 m. At this depth, the water temperature stabilised at approximately  $8^\circ\text{C}$  (Fig. 3A). Maintaining a high Cu concentration is also favoured by the low content of humic material in the water (Vanloon, Duffy 2017).

In the tested water, high average concentrations of other metals with high values of the tri-toxicity response coefficient ( $Tr_i$ ) were found,

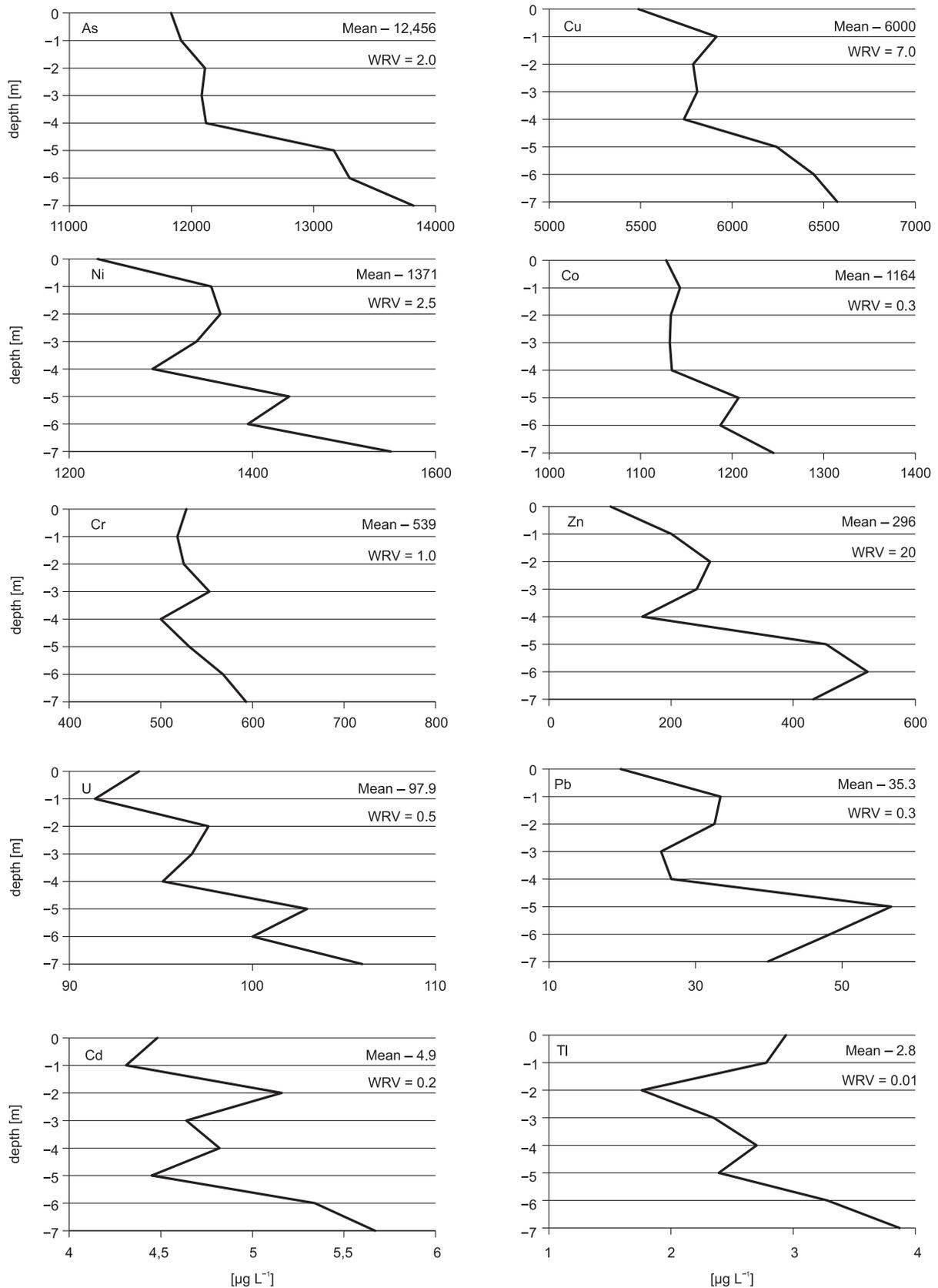


Fig. 5. Metal/metalloid concentrations in the vertical column of the mine pit lake: mean ( $\mu\text{g} \cdot \text{L}^{-1}$ ). WRV means the global water reference value [ $\mu\text{g} \cdot \text{L}^{-1}$ ] after Salminen et al. (2005).

i.e. U –  $97.9 \mu\text{g} \cdot \text{L}^{-1}$  ( $Tr_U = 40$ ) and Cd –  $4.86 \mu\text{g} \cdot \text{L}^{-1}$  ( $Tr_{Cd} = 30$ ). These values are many times greater than the geochemical background of the world's waters (Table 2) (Salminen et al. 2005), i.e. in the case of U almost 200 times, and Cd 24 times. The average contents of U and Cd in the rocks surrounding the lake, were  $3983 \mu\text{g} \cdot \text{kg}^{-1}$  and  $3571 \mu\text{g} \cdot \text{kg}^{-1}$ , respectively (after Migaszewski et al. 2007b). The specific concentrations of these elements significantly exceed the global geochemical background values in the upper continental crust, i.e.  $2.8 \mu\text{g} \text{U} \cdot \text{kg}^{-1}$  and  $0.098 \mu\text{g} \text{Cd} \cdot \text{kg}^{-1}$  (McLennan 2001). Regarding uranium, the concentration in the waters of the Podwiśniówka mine pit lake is among the highest recorded in Poland. Similar values were documented only in the waters taken from the uranium mining adits near Kowary in the Sudeten Mountains (up to  $118 \mu\text{g} \cdot \text{L}^{-1}$ ) and in the Jedlnica stream draining that area (up to  $45 \mu\text{g} \cdot \text{L}^{-1}$ ) (Chau et al. 2011). The high concentration of uranium in water is a consequence of sulphides in the surrounding rocks and their oxidation in the acidic water environment. On the other hand, cadmium concentrations in the Podwiśniówka mine pit lake are lower than the maximum values ( $74 \mu\text{g} \cdot \text{L}^{-1}$ ) found in the waters of watercourses near the Tri-State Mining District (USA) (Angelo et al. 2007).

In the group of metals showing a lower value of the toxicity index, attention should be given to the high average concentration in the water column of Ni ( $1371 \mu\text{g} \cdot \text{L}^{-1}$ ) and Co ( $1164 \mu\text{g} \cdot \text{L}^{-1}$ ). These concentrations exceeded the global reference values (Table 2 and Fig. 5) 548-fold and 3879-fold, respectively.

The average concentration of Pb in the tested water ( $35.3 \mu\text{g} \cdot \text{L}^{-1}$ ) exceeded the global reference value almost 120-fold (Fig. 5). In the rocks surrounding the lake, its content is  $16,500 \mu\text{g} \cdot \text{kg}^{-1}$  (Migaszewski et al. 2007b), which means over 450 times higher than that in the tested water.

The concentrations of Cr and Zn in the water of the Podwiśniówka mine pit lake are also higher than the global reference values (Table 2, Salminen 2005) by 539-fold and 2.8-fold, respectively. The mean concentration of Zn ( $296 \mu\text{g} \cdot \text{L}^{-1}$ ) in the water is comparable to the values found in an abandoned pyrite mine in the Rudawy Janowickie range of the Sudeten Mountains (Pociecha et al. 2017).

Table 3. Correlation matrix between metal/metalloid concentrations in water.

	As	Cu	Ni	Co	Cr	Zn	U	Pb	Cd	Tl
As	1.00									
Cu	0.95	1.00								
Ni	0.88	0.91	1.00							
Co	0.97	0.92	0.91	1.00						
Cr	0.77	0.75	0.72	0.72	1.00					
Zn	0.90	0.93	0.80	0.82	0.68	1.00				
U	0.93	0.82	0.86	0.90	0.72	0.82	1.00			
Pb	0.77	0.81	0.70	0.74	0.35	0.90	0.68	1.00		
Cd	0.67	0.63	0.61	0.55	0.70	0.55	0.66	0.23	1.00	
Tl	0.61	0.58	0.43	0.63	0.64	0.34	0.38	0.15	0.47	1.00

Significance level ( $p$ ): green – 0.01; yellow – 0.05; orange – 0.1; white – non-significance.

In the Podwiśniówka mine pit lake, the lowest average concentration is found for Tl ( $2.8 \mu\text{g} \cdot \text{L}^{-1}$ ). Although this might appear to be a low concentration, a comparison with the global reference value results in the discovery that it is characterised by an excess of 280 times (Table 2). The maximum concentration of this metal in the bottom layer of water was  $3.9 \mu\text{g} \cdot \text{L}^{-1}$ . Similar concentrations of Tl ( $1.9$ – $8.1 \mu\text{g} \cdot \text{L}^{-1}$ ) were found in the watercourse flowing out of the Xingren Hg-Tl mine in Guizhou Province, China, as well as in the water from the Gaofeng River ( $0.5$ – $9.1 \mu\text{g} \cdot \text{L}^{-1}$ ) located downstream of the mining site (Liu et al. 2019). The presence of thallium in surface waters is closely related to sulphide minerals, especially in mines (Peter, Viraraghavan 2005). Thallium is highly toxic, and comparable in toxicity to lead and mercury (Kemper, Bertram 1991).

Relationships between the contents of particular elements in the water result from their geochemical features. The correlation coefficient between particular pairs (45) of metals in water ( $N = 8$ ) is statistically significant at the level of  $\alpha = 0.1$ , and for 12 pairs, it is non-significant (Table 3). The correlation coefficient at a significance level of  $\alpha = 0.01$  indicates a very strong relationship between analysed data pairs. The most significant positive correlations are between As and Co ( $R = 0.97$ ), Cu ( $R = 0.95$ ) and U ( $R = 0.93$ ) and between Cu and Zn ( $R = 0.93$ ). A lower level of statistical significance (with a  $p$  value  $< 0.05$ ) and non-significance was discovered by analysing only the relationship between Tl content and the concentrations of other metals (Table 3).

## Pollution indices

The pollution index value (Table 4) ranges are as follows: As (5916–6909), Co (3760–4150), U (182.8–212.0), Cu (784.1–939.1), Tl (176–387), Ni (492.4–620.4), Cr (500–593), Cd (21.6–28.4), Pb (66–189) and Zn (5.1–26.1). It follows that As and Co are the main contaminants in the water body under study, with extremely high SPI values.

Using cluster analysis, a dendrogram was developed, based on which two depth intervals were distinguished, with the most significant taxonomic distance considering the SPI for 10 given metals/metalloids (Fig. 6). The first group covers depths from 0 m to 4 m (five divisions), where the geochemical characteristics of the near-surface layer water (0 m) and at a depth of 4 m show the greatest statistical similarity. This indicates water mixing in this zone, i.e. above the chemocline. The second group consists of three depth levels:

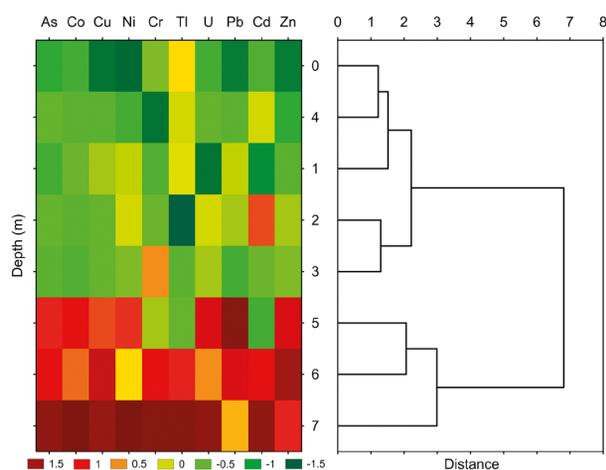


Fig. 6. Heatmap for hierarchical clustering of the single pollution index (SPI) in the vertical water column.

5 m, 6 m and 7 m. The graphical effect of the SPI variation in the vertical water column is shown in the heatmap provided in Fig. 6. The heatmap demonstrates a distinct zone for lower SPI values, where most metals show values  $\leq 0$ , and are thus represented by the colours green and yellow, and another distinct zone for higher SPI values, where metals showing positive values are represented by shades of red. The intensity of the shades of red (SPI increase) increases with depth, where it reaches its highest values in the bottom zone of the pit lake for almost all metals (except Pb and Zn) (Fig. 6).

Out of 10 tested metals/metalloids, in all cases, the average SPI value in the water column exceeds the very strong level of pollution ( $SPI \geq 5$ ) commonly used in the literature (including Lian, Lee 2021). Record high SPI values are achieved by As and Co ( $6271 \pm 356$  and  $3879 \pm 137$ ). The lowest value of SPI was observed for Zn ( $14.8 \pm 7.2$ ) (Fig. 7).

An analysis of the pollution index (IPI) for multiple elements in the water column offers noteworthy results (Table 4). Its average IPI value – 1272 – is exceptionally high and exceeds

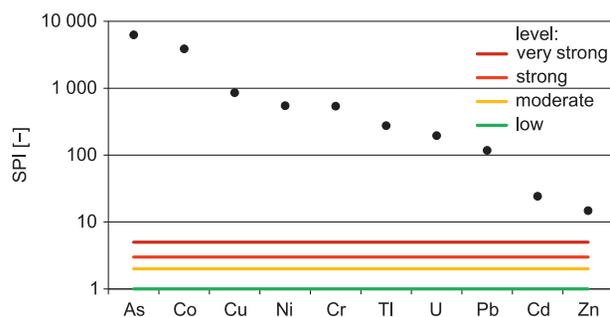


Fig. 7. Single pollution index (SPI) for heavy metals/metalloids.

Table 4. The results of the single pollution index (SPI) calculations for given metals/metalloids in the vertical column of the pit lake against mean values and standard deviations (SD). IPI – integrated pollution index.

Depth [m]	SPI										IPI
	As	Co	Cu	Ni	Cr	Tl	U	Pb	Cd	Zn	
0	5916	3760	784.1	492.4	528.0	294.0	187.6	66.0	22.4	5.1	1206
1	5957	3810	844.9	542.0	518.0	278.0	182.8	111.3	21.6	10.1	1228
2	6055	3777	826.7	546.0	525.0	176.0	195.2	108.7	25.8	13.2	1225
3	6041	3773	829.9	535.6	553.0	235.0	193.4	84.3	23.2	12.1	1228
4	6059	3780	819.6	516.4	500.0	270.0	190.2	89.0	24.1	7.7	1225
5	6583	4023	891.7	576.0	531.0	239.0	206.0	189.0	22.3	22.7	1328
6	6648	3957	920.7	558.0	568.0	328.0	200.0	161.3	26.7	26.1	1339
7	6909	4150	939.1	620.4	593.0	387.0	212.0	133.0	28.4	21.7	1399
Mean	6271	3879	857.1	548.4	539.5	275.9	195.9	117.8	24.3	14.8	1272
SD	356.1	137.2	50.6	36.1	28.0	59.6	9.1	38.7	2.3	7.2	67.7

254 times the highest accepted level (very strong pollution  $\geq 5$ ). Two metals/metalloids determine the high IPI values, As and Co, and their share reaches 79.8% of the total value of the IPI, with the former accounting for 49.3% (Fig. 8). Up to a depth of 4 m, its differentiation is relatively small (1206–1228), but below 5 m, there is an abrupt increase to 1328, reaching 1399 in the bottom layer (Fig. 9). After introducing a second (upper) X-axis representing EC, the intersection of the lines showing both features at a depth of just below 4 m is noticeable. This indicates the presence of a barrier to water mixing and circulation, even

though the tests were carried out in the autumn period with increased water circulation.

## Conclusions

The Podwiśniówka mine pit lake (area 1.5 ha, max. depth 7.0 m) was created in 2014 after the quarrying operations—involving the quarrying of Cambrian quartzite sandstones and sandstones with pyrite veins, in which Migaszewski et al. (2007b) found a very high concentration of trace elements (including As, amounting to  $3050 \text{ mg} \cdot \text{kg}^{-1}$ ) – that had been taking place in the region came to an end. Tests carried out in the water column (in the central part of the lake) showed the presence of water with a strongly acidic reaction ( $< 2.3 \text{ pH}$ ), a high concentration of sulphates ( $\text{SO}_4^{2-} > 3000 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ ) and high electrolytic conductivity, increasing towards the bottom ( $> 6500 \text{ } \mu\text{S} \cdot \text{cm}^{-1}$ ). The water was found to be polluted with various trace elements that largely exceeded the geochemical background and safe limit (for drinking water) suggested by the WHO. High concentrations of the 10 tested trace elements were found in the following sequence:  $\text{As} > \text{Co} > \text{U} > \text{Cu} > \text{Tl} > \text{Ni} > \text{Cr} > \text{Cd} > \text{Pb} > \text{Zn}$ . An extremely high concentration (one of the largest in the world) was found for arsenic (at the surface –  $11,833 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ , at the bottom –  $13,818 \text{ } \mu\text{g} \cdot \text{L}^{-1}$ ). The concentrations of all analysed elements generally show an increasing tendency with water depth.

The study uses the single pollution index (SPI), a useful and frequently used diagnostic tool for assessing the condition of various components of the environment, but one characterised by a minimal frequency in relation to deployment in applications involving water. The SPI for each element (SPI, mean) is ranked as follows:  $\text{As} (49.3\%) > \text{Co} (19.0\%) > \text{Cu} (6.7\%) > \text{Ni} (4.3\%) > \text{Cr} (4.2\%) > \text{Tl} (2.2\%) > \text{U} (1.6\%) > \text{Pb} (0.9\%) > \text{Cd} (0.18\%) > \text{Zn} (0.12\%)$ . The average SPI value in the water column of all tested metals/metalloids exceeded a very strong level of pollution ( $\text{SPI} \geq 5$ ). The integrated pollution index (IPI) in the water column increases with depth (from 1206 to 1399), creating two distinct depth zones: upper (0–4 m) and lower (5–7 m). The average value is exceptionally high on a global scale ( $\text{IPI} = 1272$ ) and more than 254 times the highest (very strong) reference level, as mentioned in the literature.

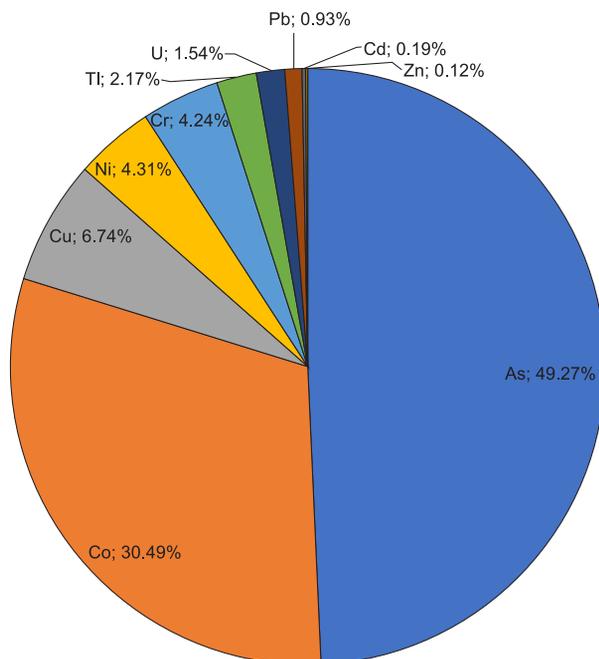


Fig. 8. Share of individual metals/metalloids in the integrated pollution index (IPI).

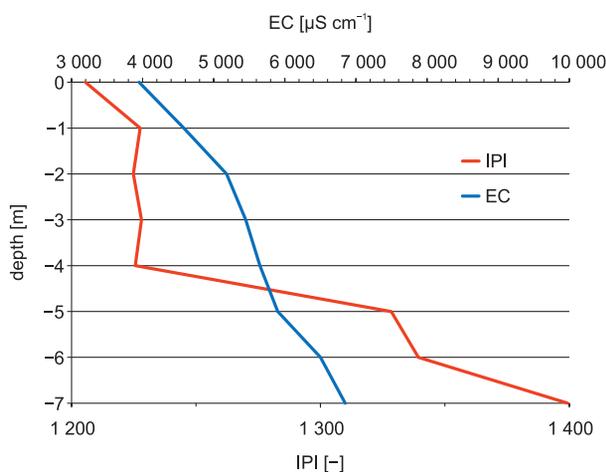


Fig. 9. Integrated pollution index (IPI) and electrical conductivity (EC) in the vertical water column.

The causative factors underlying the lack of living organisms in the tested water reservoir can probably be identified as the extremely high concentrations of the described trace elements (toxicity response coefficient:  $Tr_U = 40$ ,  $Tr_{Cd} = 30$ ,  $Tr_{As, Ti} = 10$ ,  $Tr_{Co, Cu, Ni, Pb} = 5$ ) and the calculated values of water pollution indices. This reservoir has been identified as a local ecological threat.

The results of the research presented in earlier studies (Migaszewski et al. 2018b, 2019) and in the present one clearly indicate that the water in the Podwiśniówka acid mine pit lake could pose serious problems by way of the causation of environmental pollution in the immediate vicinity, which is why, to eliminate this identified threat, the management of the Wiśniówka quarrying area involves the undertaking of a variety of activities for the control and reduction of acidic pollution. The remediation strategy used here was neutralisation of highly acidified lake waters with the use of calcium carbonate. Similar solutions to eliminate hazards in this type of lake are used worldwide (Kefeni et al. 2017). After water neutralisation, the pit was covered with sandstone, and the water reservoir was liquidated.

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### Author's contribution

Conceptualization: R.S., T.C. and T.M.; methodology: R.S., T.C. and T.M.; formal analysis: R.S., T.C. and T.M.; investigation: R.S., T.C. and T.M.; writing – original draft preparation: R.S., T.C. and T.M.; writing – review and editing: R.S., and T.C.; visualization: R.S.

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